

Constraints on urban VOC emissions from day of week measurements of column NO₂

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Introduction

The ratio of column NO₂ observed on weekdays to that observed on weekends (i.e., the NO₂ weekend effect) has been used extensively to constrain NO_x emissions from sources that do not operate on weekends. For instance, ~40 % less NO₂ is observed on the weekend by OMI over the Los Angeles Basin (~150 x 100 km²) indicating the reduction of heavy-duty diesel emissions on the weekends. The decreases also depend on OH and PAN formation as they affect the NO_x lifetime. We show that agreement between simulation and observation both with respect to magnitude and spatial pattern of weekend changes is qualitatively improved when emissions of hydrocarbons (VOCs) are increased.

Conclusions

- OMI observes large day-of week differences in column NO₂ over Los Angeles with sufficient spatial resolution to observe that the decreases are non-uniform
- Using simulations, we show that the weekend effect in NO₂ contains chemical information about VOC emission rate
- In these WRF-CHEM simulations, we identify that decreases in weekend NO₂ are due to a decrease of NO_x emissions, an increase in OH (decrease in NO₂ lifetime) and an increase in the amount of NO_x stored as PAN

Acknowledgements

This work was supported by NASA (grant NNX08AE566 and NASA Earth and Space Science Fellowship program) and CARB (grant 06-328).

OMI observations of the NO₂ Weekend Effect

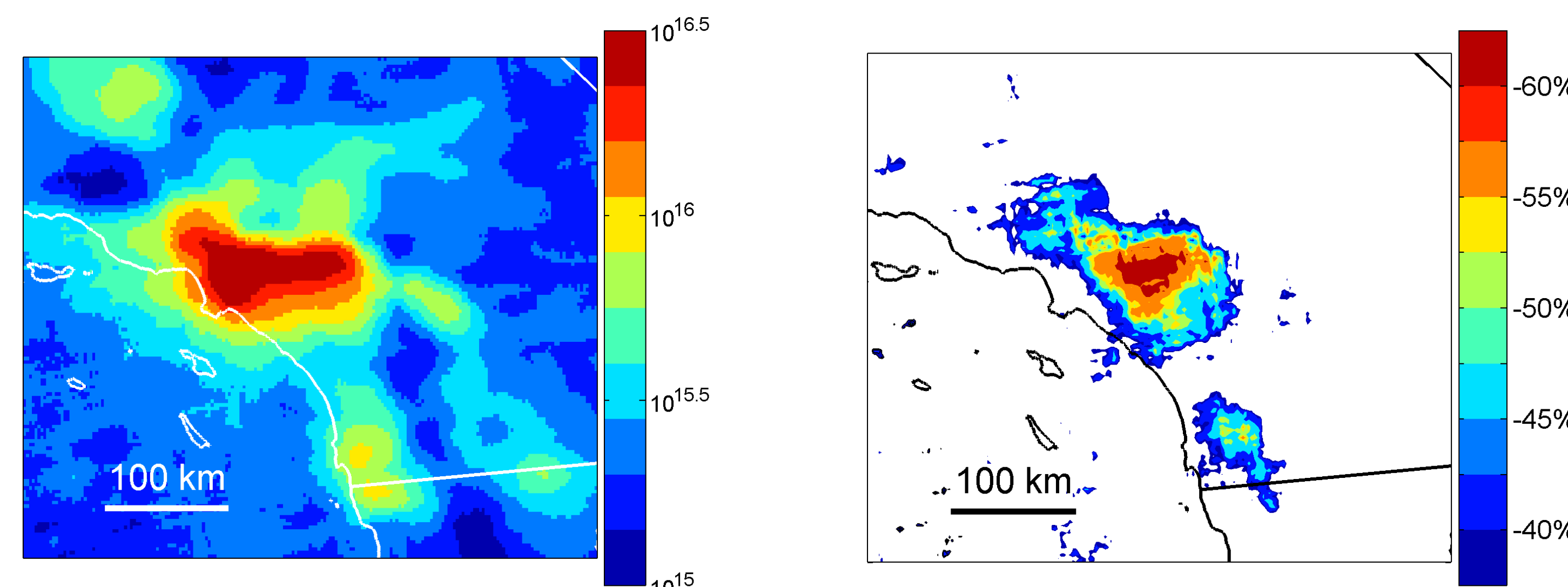


Figure 1. a) Weekday 2005-2008 May, June, July area-weighted average column NO₂ (molecules cm⁻²) and **b)** the ratio of weekday to weekend column NO₂. Values in *b* are not shown where decreases are less than 37.5 %.

WRF-CHEM Simulations of the NO₂ “Weekend Effect”

Setup: For Southern California, we use WRF-CHEM run at 4 km resolution to simulate weekday column NO₂ (*fig. 2- far left*), the NO₂ “weekend effect” ($0.625 \times \text{ENO}_x\text{-Weekday} = \text{ENO}_x\text{-Weekend}$; $\text{E}_{\text{VOC}}\text{-Weekday} = \text{E}_{\text{VOC}}\text{-Weekend}$ *fig. 2-mid left*), and the resulting “weekend effect” of PAN, OH, and PAN:NO₂ ratio (*fig. 2-right*) along a transect of the LA basin for June 10-24, 2006. Simulations are run at low (1x NEI2005, *fig. 2-top*), moderate (2x NEI2005, *fig. 2-middle*) and high (4x NEI2005, *fig. 2-bottom*) VOC emissions. At highest VOC emissions (*bottom*), emissions of NO_x were increased by 20% versus low and moderate VOC scenarios in order to maintain agreement of weekday column NO₂ (*fig. 2-left*)

• Previous studies and bottom-up inventories suggest that NO_x emissions decrease by ~40% on weekends over Los Angeles

• The corresponding OMI-observed decrease in column NO₂ (weekday, *fig. 1-left*) varies dramatically in space (*fig 1-right*) with decreases of as much as 62.5%.

• The maximum relative weekend decrease (*fig. 1c*) is ~100 km downwind of observed weekday maximum in column NO₂ (*fig. 1a*)

Results: WRF simulations produce an NO₂ “weekend effect” that is non-uniform with weekend decreases that are large and varied across the LA basin. Non-linear weekend decreases (> 37.5 %) are observed in all three VOC emission scenarios (*fig. 2- mid right*), but are much larger (> 60 %) and occur closer to the source region at moderate and high VOC emissions (*fig. 2-middle and bottom*) resulting in much better qualitative agreement with observation (*fig. 1b*)

Analysis: Feedback of NO₂ on OH and consequent feedbacks of OH on the PAN to NO₂ ratio are co-located with the large weekend decreases of NO₂ (> 37.5%, *fig. 2-mid right, red line*). The large day of week differences in the PAN:NO₂ ratio downwind of Los Angeles depend strongly on VOC emission rate (*fig. 2-far right*)

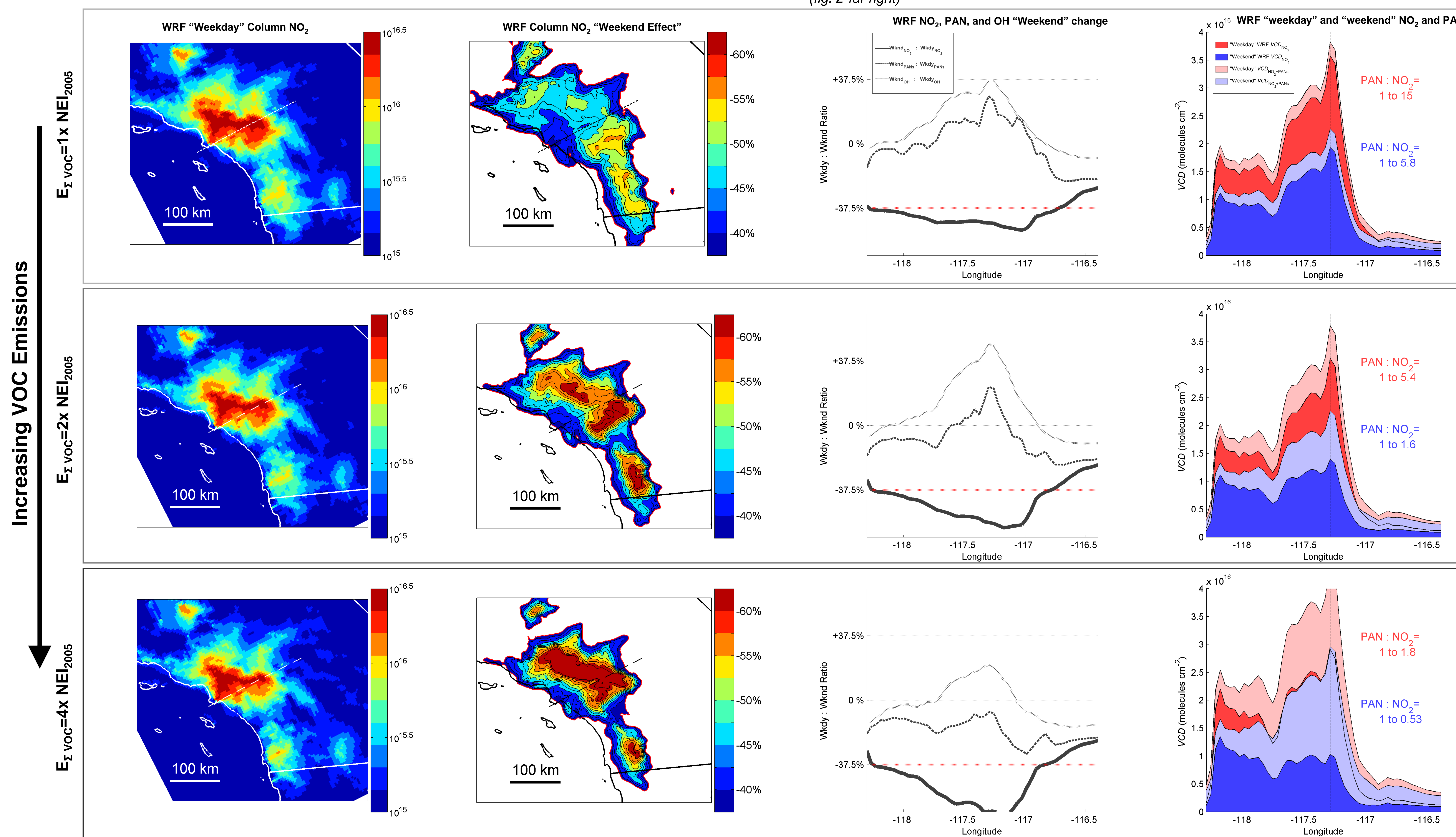


Figure 2. WRF-CHEM simulation with standard (*top*, $\text{E}_{\text{VOC}}=1\text{x}$ and $\text{E}_{\text{NO}_x\text{-wkdy}}=1\text{x}$ NEI2005), 2x standard (*middle*, $\text{E}_{\text{VOC}}=2\text{x}$ and $\text{E}_{\text{NO}_x\text{-wkdy}}=1\text{x}$ NEI2005), and 4x standard VOC emissions (*bottom*, $\text{E}_{\text{VOC}}=4\text{x}$ and $\text{E}_{\text{NO}_x\text{-wkdy}}=1.2\text{x}$ NEI2005) over Southern California for June 10-24, 2006 of “weekday” column NO₂ (*far left*) and the ratio of “weekday” to “weekend” column NO₂ (*mid left*). Values are not shown where decreases are less than 37.5% (i.e. greater than the percentage decrease in NO_x emissions). The simulated weekend effect of NO₂ (*solid line*), PAN (*dashed line*), and OH (*dotted line*) (*mid right*) and the profile of weekday PAN:NO₂ ratio (*far right*) are shown for a transect of the LA Basin highlighted in the images.